



TITLE:

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CITATION:

Zeng, Chenghui ...[et al]. Impact of feed water pH and membrane material on nanofiltration of perfluorohexanoic acid in aqueous. Chemosphere 2017, 183: 599-604

ISSUE DATE:

2017-09

URL:

<http://hdl.handle.net/2433/245419>

RIGHT:

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1 Impact of Feed Water pH and Membrane Material on Nanofiltration of Perfluorohexanoic Acid

2 in Aqueous Solution

3

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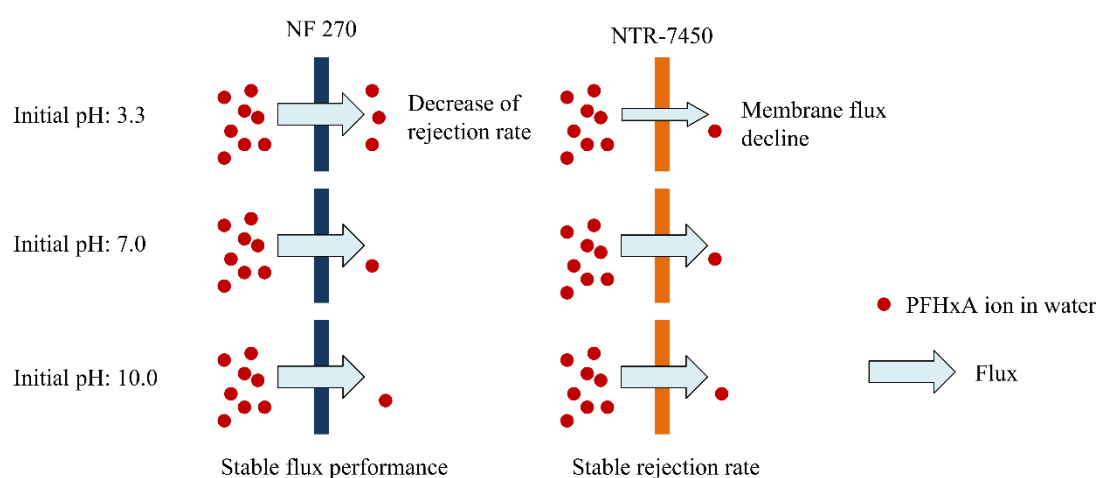
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9 Graphical abstract



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16 **Highlights**

- 17 ● PFHxA in aqueous solution was concentrated by two kinds of NF membranes.
- 18 ● Polyamide and sulfonated polyethersulfone NF membranes were used.
- 19 ● Feed water pH showed different impact on these two kinds of NF membranes.
- 20 ● The membrane flux or PFHxA rejection rate deteriorated at acidic pH.
- 21 ● Increasing the pH can enhance flux and rejection performance of NF membranes.
- 22

23 **Abstract**

24 Nanofiltration was thought to be a good option for the recovery of perfluorohexanoic acid (PFHxA)
25 from industrial wastewater. In this study, two commercially available nanofiltration (NF)
26 membranes (NF 270 and NTR-7450) were tested to concentrate the PFHxA in aqueous solution.
27 Filtration test was conducted in crossflow filtration mode. Membrane flux and PFHxA rejection rate
28 were monitored throughout the filtration test. The impact of initial feed water pH on membrane
29 performance was investigated. Results demonstrated that the two NF membranes showed different
30 response to the change of initial feed water pH, which was caused by the intrinsic properties of
31 membrane material. The flux performance of NF 270 was stable, while its rejection rate of PFHxA
32 was very sensitive to the change of initial feed water pH. Opposite result was obtained with
33 NTR-7450. It has a very good stability on rejection rate, while its flux is very sensitive to the change
34 of initial feed water pH. The mechanisms behind these phenomena were also discussed. The results
35 obtained in this study should be very useful for the process design in practical engineering.

36

37 **Keywords:** perfluorohexanoic acid (PFHxA), recovery, nanofiltration (NF), polyamide membrane,
38 sulfonated polyethersulfone membrane , pH

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a group of anthropogenic compounds, which have been widely used in industries due to their unique characteristics, such as surface activity, thermal and chemical stability, etc (Herzke et al., 2012; Wang et al., 2013). These compounds have been detected in the environment ubiquitously, including wastewater treatment plants, water purification plant, lakes, sea water and even arctic area, etc (Kunacheva et al., 2011; Yu et al., 2013; Rahman et al., 2014; Lu et al., 2015; Guo et al., 2016). In recent years, they have received continuously increasing concern as they found to be toxic, persistent and bioaccumulative (Kannan et al., 2004; Yeung et al., 2006; Fujii et al., 2007; Svihlikova et al., 2015). Industrial discharge was considered as one of the main sources of PFASs pollution in water environment (Prevedouros et al., 2006). In order to provide protection to human health and environment, governments and international organizations have been involved in phasing out the production and use of PFASs globally (ECHA, 2013; US EPA, 2006). PFASs-related industries are also seeking cost-effective techniques on the recovery of PFASs from industrial wastewater so that the discharge of PFASs to the environment could be reduced. Membrane technology has been thought to be a good option for the recovery of PFASs from industrial wastewater (Tang et al., 2006; Tang et al., 2007).

Among all membranes ranging from reverse osmosis (RO) to microfiltration (MF), nanofiltration (NF) membrane has a molecular weight cut-off ranging from 200 to 1,000 Da. It offers higher flux

61 than reverse osmosis (RO) and better retention performance than ultrafiltration (UF) for treating
62 wastewater containing small molecule. These advantages make NF membrane became very
63 promising in the recovery of PFASs from industrial wastewater. Before, most of the researches had
64 focused on rejecting PFOA and PFOS (C8) by NF or RO membrane as they were the main kinds of
65 PFASs used in industries (Tang et al., 2006; Tang et al., 2007; Zhao et al., 2013; Hang et al., 2015;
66 Zhao et al., 2016). As the regulations and legislation on the use and manufacture of PFOA and
67 PFOS become more stringent, some industries have shifted to use the shorter chain PFASs as the
68 alternative (Wang et al., 2013; Wang et al., 2017). For example, a type of short chain PFASs-
69 perfluorohexanoic acid ($\text{CF}_3(\text{CF}_2)_4\text{COOH}$, PFHxA)- has been detected in water environment with its
70 concentration as high as 16,000 ng/L (Takemine et al., 2014), which suggest that some industries have
71 started to use PFHxA as the alternative of PFOS and PFOA. PFASs with different chain lengths have
72 different physicochemical properties (Rahman et al., 2014). Thus, membrane's rejection properties to
73 them might be also different. However, limited information on rejection of PFHxA by NF membranes
74 is available.

75
76 A typical structure of NF membrane consists of three parts: top selective layer, microporous
77 substrate and nonwoven fabric. The separation properties of NF membrane mostly depend on the
78 selective layer. Generally, the selective layer of commercialized NF membranes was made from two
79 types of materials. One is polyamide (PA) and another one is sulfonated polyethersulfone (SPES).

These two kinds of membranes showed different response to the change of feed water pH (Mänttari et al., 2006). Thus, they might also have different rejection properties to PFHxA in water. Furthermore, most of the previous researches were conducted with a PA membrane - NF 270 (Filmtech, USA), which showed a relatively high flux and salt rejection rate among commercialized NF membranes (Tang et al., 2009). The rejection properties of SPES NF membrane to PFHxA in wastewater were still not well investigated.

This paper describes an investigation on the recovery of PFHxA in pure water by both PA and SPES NF membrane. The impact of pH on PFHxA rejection rate and membrane flux was investigated. PFHxA aqueous solution was used and pH of the feed water was adjusted by NaOH. Filtration test was conducted in crossflow filtration mode. PFHxA concentration in water samples was measured by High-performance Liquid Chromatography coupled with tandem mass spectrometer (1200 series, HPLC/MS/MS, Agilent Technologies, USA).

2. Materials and Methods

2.1 Chemicals and Materials

2.1.1 Chemicals

All chemicals used for PFHxA analysis were of HPLC/MS/MS grade unless otherwise specified. Perfluorohexanoic acid, methanol, acetonitrile, ammonium acetate solution (1 mole/L) were purchased

from Wako Pure Chemical (Japan). Milli-Q water purified by PresepC-Agri (C18) cartridge (Wako, Japan) and Oasis®HLB cartridge (Waters, Japan) was used as the solvent for PFHxA analysis in order to avoid PFASs contamination.

2.1.2 NF membranes

Two membranes were used in this study: NTR-7450 was purchased from Nitto Denko (Japan) through Membrane Soltech (Japan), NF 270 was supplied by Dow/Filmtech (USA) through Mikuniki (Japan). NTR-7450 was obtained and stored as dry coupons, while NF 270 was supplied and stored in water. All the coupons were stored in refrigerator (5 °C) once arrived to our lab. The information of these two membranes were summarized in **Table 1**.

Table 1 Characteristics of membranes used in this research

Membrane	NF 270	NTR-7450
MWCO (Da) ^(a)	200	600 - 800
zeta-potential at pH 7.0 (mV) ^(a)	− 21.6	− 16.6
Pure water permeability (m ³ /(m ² ·MPa ¹ ·d ¹))	3.92	2.62
NaCl rejection rate (%)	58	55
Material of selective layer	polyamide	sulfonated polyethersulfone
Contact angle (°)	32.6 ± 1.3 ^(b)	69.6 ± 5.9 ^(c)
Manufacturer	FilmTech, USA	Nitto Denko, Japan

(a) The molecular weight cut-off (MWCO) of membrane, zeta-potential were obtained from literature (Braeken et al., 2006); (b) Contact angle of NF 270 was adopted from (Tang et al., 2009); (c) Contact angle of NTR-7450 was adopted from (Boussu et al., 2005); (d) The pure water permeability and NaCl rejection rate were measured in this study. The test conditions for NaCl rejection rate measurement: NaCl 2000 mg/L, 1 L/min and 0.7 MPa. The experimental set-up was the same with filtration experiment.

2.2 Experimental set-up and filtration test

2.2.1 Experimental set-up

The experimental set-up consisted of two customized membrane test set-ups (FTU-1 and C-10T) purchased from Membrane Soltech, Japan. More details of these two set-ups can be found on the website of manufacturer (Membrane SolTech. 2017). The whole system was schematically described in **Fig. 1**. Basically, it has four parts: feed tank, permeate tank, diaphragm pump and membrane cell.

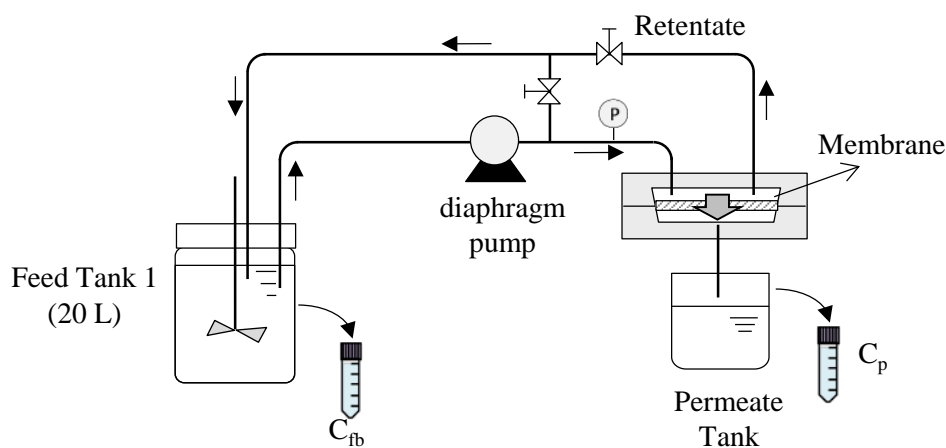


Fig. 1 Membrane testing set-up

All of them were made from non-PFASs adsorptive material. The feed water was pumped into the membrane cell by a diaphragm pump. The transmembrane pressure (TMP) and crossflow rate were kept at 1 L/min and 0.7 MPa, respectively, by adjusting the bypass valve manually throughout the whole filtration test. Permeate was discharged to the permeate tank directly and the retentate was recycled back to the feed tank. The solutes in feed tank were concentrated throughout the filtration test.

133 The whole membrane set-up was put in an air-conditioned room so the feed water temperature was
134 almost kept constant (29 – 30 °C) during the filtration test.

135

136 2.2.2 Filtration test

137 In this study, synthetic wastewater prepared by adding PFHxA into the pure water was used for the
138 filtration test. Pure water was supplied by an ion exchanger system (Kurita MD-05, Japan), in which
139 most of the matrix in tap water was removed. The initial concentration of PFHxA in synthetic
140 wastewater was about 100 mg/L, which is a typical concentration for PFHxA in industrial wastewater
141 (Karnwadee W., 2015). For each filtration test, 20 L synthetic wastewater was added into the feed tank.
142 Also, a new membrane coupon (60 cm²) was used, which was pretreated by filtration with pure water
143 at 0.7 MPa for at least 1 hour. In order to know the impact of initial feed water pH on membranes
144 performance, the filtration tests were conducted with feed water at three initial pH values: pH 3.3
145 (only PFHxA was added), pH 7.0 (addition with PFHxA and NaOH) and pH 10.0 (addition with
146 PFHxA and NaOH).

147

148 Throughout the filtration, membrane flux, pH, temperature were monitored. Membrane flux was
149 measured gravimetrically by weighing the mass of permeate collected at predetermined intervals. pH
150 of feed and permeate was monitored by B-172 pH meter (Horiba Ltd., Japan). Temperature was
151 measured by CT-300WP digital thermal meter (Custom Corp., Japan). To obtain the rejection rates of

152 PFHxA, the feed and permeate samples were collected continuously throughout the whole filtration
153 test. The overall rejection rate of PFHxA by membrane was calculated by following equation:

154

$$155 \quad \text{Rejection rate (\%)} = (1 - C_p/C_f) \times 100 \quad (1)$$

156 Where C_p is the concentration of PFHxA in permeate (mg/L);

157 C_f is the concentration of PFHxA in feed (mg/L).

158

159 In this study, normalized flux was used to evaluate the change of membrane flux throughout the
160 filtration test. It was defined as:

161

$$162 \quad \text{Normalized flux (\%)} = Q_t \times 100/Q_0 \quad (2)$$

163 Where Q_t is the membrane flux at filtration time t (m/d);

164 Q_0 is the membrane flux at the beginning of filtration (m/d).

165

166 **2.3 Analytical method for PFHxA**

167 HPLC/MS/MS was used for PFHxA analysis. In this study, both feed and permeate samples were
168 diluted by 40% acetonitrile solution to a desired concentration before analyzing by HPLC/MS/MS.

169 Chromatographic separation was conducted on a Zorbax Eclipse Plus C18 (Agilent Technologies,
170 USA) and the column temperature was set at 40 °C. The mobile phase used in this study was a

171 mixture of solvent A (acetonitrile) and B (5 mmol/L ammonium acetate) and the flow rate was set at
172 0.25 mL/min. The eluent started from 30% solvent A, increased to 45% at 1.0 min, then 60% at 4
173 min, held at 60% for 0.5 min, went up to 90% at 4.5 min, kept at 90% for 3.5 min, and then ramped
174 down to 30%. The post time was 5 min and the total running time for one sample was 13 min. Triple
175 Quadrupole (Agilent Technologies, USA) mass spectrometer (MS/MS) was used for quantitative
176 analysis. Mass spectrometer was operated with the electrospray ionization (ESI) in negative mode.
177 Analyte ion was monitored by using multiple reaction monitoring (MRM) mode. The m/z for parent
178 ion and daughter ion were 313 and 269, respectively. Collision energy was set at 2 V.

179

180 **3. Results and discussions**

181 **3.1 Rejection rates of PFHxA by two membranes**

182 In order to investigate the impact of initial feed water pH on the rejection rates of PFHxA by NF
183 membranes, a series of experiments was carried out with feed water at different pH. In **Fig. 2**, the
184 rejection rates of PFHxA by NF 270 and NTR-7450 under different test conditions were shown.
185 When only PFHxA was added into the feed tank (initial pH: 3.3), the rejection rate of PFHxA by NF
186 270 was quite low. Initially, the rejection rate of PFHxA was around 87%. Then, it started to
187 decrease along with the concentration increase in feed tank. Finally, it kept constant at about
188 71%. This was confirmed by the result obtained in a repeated experiment. However, when the initial
189 pH of feed water was adjusted to 7.0 by adding NaOH solution, the initial rejection rate of PFHxA

by NF 270 increased to 96%. When the feed concentration of PFHxA became higher than 400 mg/L, rejection rate was enhanced further (>98%). After increasing initial pH of feed water to 10.0, the rejection rate of PFHxA by NF 270 also increased further. The initial rejection rate was 97% initially and maintained at 99% at last. Based on above discussions, it can be concluded that NF 270 could reject the PFHxA in pure water more effectively at neutral or alkaline conditions than that at acidic conditions. However, for NTR-7450, its rejection rate to PFHxA seems much less sensitive to the change of initial pH of feed water. Under all three pH conditions tested, the rejection rates were maintained above 96%.

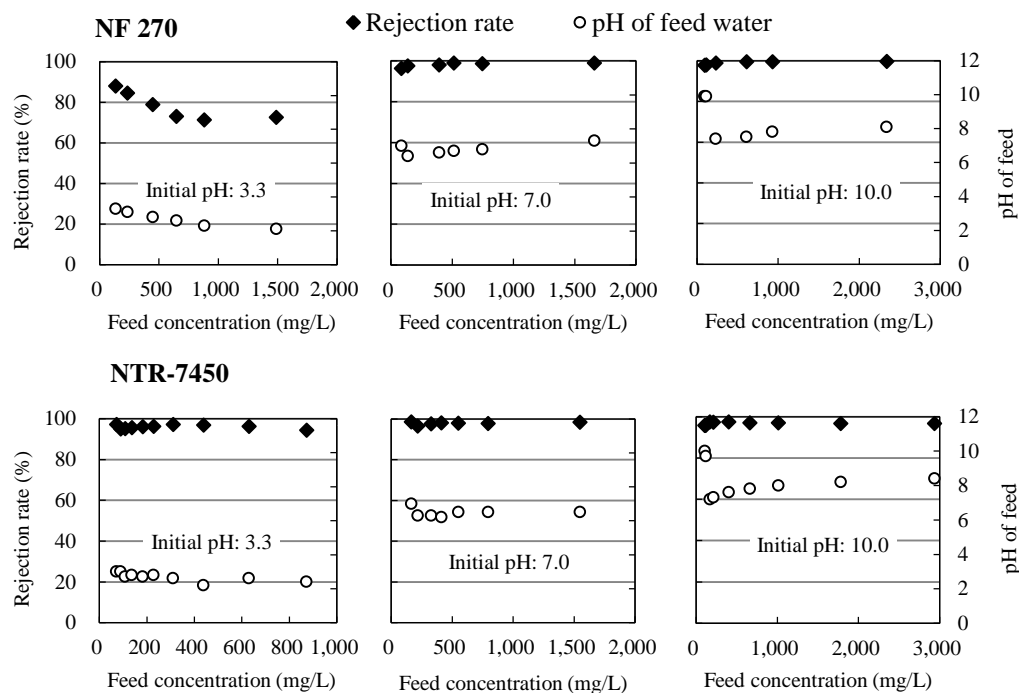


Fig. 2 The rejection rates of PFHxA by NF 270 and NTR-7450 throughout the filtration tests at different initial feed water pH conditions

204 According to the information shown in **Table 1**, NF 270 is tighter than NTR-7450. However, its
205 rejection rate to PFHxA was lower than that of NTR-7450 at acidic condition (pH: 3.3). This
206 suggested that the rejection mechanism of PFHxA by NF membranes was not just dependent on the
207 size exclusion. The interaction between PFHxA and membrane surface might also play an important
208 role. Additionally, NF 270 also showed a higher sensitivity to the change of initial feed water pH
209 than NTR-7450. This could be explained by the change of interaction between PFHxA and
210 membrane surface at different initial feed water pH. On one hand, PFHxA is a kind of strong acid
211 and has pKa value of -0.16 (Steinle-Darling and Reinhard, 2008). When only PFHxA was added into
212 the feed water (initial pH: 3.3), it can present in water by both ionic ($\text{CF}_3(\text{CF}_2)_4\text{COO}^-$) and non-ionic
213 ($\text{CF}_3(\text{CF}_2)_4\text{COOH}$) form. When initial feed water pH was adjusted to 7.0 or 10.0, PFHxA could
214 dissociate almost completely. On the other hand, the surface charge of NF membrane could also be
215 changed at different pH. Thus, the interaction between PFHxA and membrane surface charge may
216 change at different pH.

217

218 For NF 270, its selective layer was made from polyamide, which possesses dissociable carboxylic
219 and amine groups. According to the data reported by Mänttari et al., 2006, this membrane has an
220 isoelectric point (IEP) between pH 5.0 and pH 6.0. At pH below 5.0, the amine functional groups on
221 membrane surface would protonate ($\text{=NH}_2 \rightarrow \text{=NH}_3^+$) and resulted in positive charge. At pH above

222 6.0, the carboxyl groups on membrane surface would deprotonate ($\equiv\text{COOH} \rightarrow \equiv\text{COO}^-$) and resulted
223 in negative charge.

224

225 When the initial pH of feed water was at 3.3, membrane surface of NF 270 was positively charged
226 as a result of protonation of amine groups. The electrical repulsion did not happen between PFHxA
227 ion and membrane surface charge. On the contrary, PFHxA ion might even be adsorbed onto the
228 membrane surface due to the electrostatic attraction between the hydrophilic charged head group of
229 PFHxA (R-COO^-) and membrane surface charge. Once the charged head group of PFHxA ion was
230 adsorbed onto the membrane surface of NF 270, the hydrophobic tail of PFHxA ion would be
231 oriented towards the aqueous phase, which made the membrane surface became more neutral. Thus,
232 PFHxA ion can pass through membrane easily and resulted in a relatively low rejection rate of
233 PFHxA. However, when the initial pH of feed water was increased to 7.0 and 10.0, the membrane
234 surface of NF 270 became negatively charged as a result of deprotonation of carboxyl groups.
235 Electrical repulsion between PFHxA ion and membrane surface took place and lead to high rejection
236 rate to PFHxA.

237

238 For NTR-7450, its selective layer was made from sulfonated polyethersulfone and the functional
239 group on selective layer is sulfonate group ($-\text{SO}_3\text{H}$). This membrane can only be negatively charged,
240 which was proved by its zeta-potential measured by Mänttari et al., 2006. Thus, electrical repulsion

241 between PFHxA ion and membrane surface charge took place at all pH conditions tested. When the
242 initial feed water pH was 3.3, PFHxA in feed water could be in ionic ($\text{CF}_3(\text{CF}_2)_4\text{COO}^-$) and
243 non-ionic ($\text{CF}_3(\text{CF}_2)_4\text{COOH}$) form. Electrical repulsion alone might not be able to reject the PFHxA
244 effectively as non-ionized PFHxA cannot be repelled by membrane surface charge. But the rejection
245 rate of PFHxA was still higher than 96%. This could be explained by the shrinkage of membrane. At
246 acidic conditions, the dissociation of sulfonate group was depressed and resulted in less electrical
247 repulsion inside membrane “pores”. Thus, the shrinkage of membrane happened. This made the
248 “pore size” of NTR-7450 became smaller and the rejection rate of PFHxA was enhanced. When the
249 initial feed water pH was 7.0 and 10.0, the sulfonate groups on selective layer were dissociated and
250 membrane surface became negatively charged. Meanwhile, PFHxA was also ionized at neutral and
251 alkaline conditions. Thus, PFHxA could be rejected via electrical repulsion.

252

253 Another interesting finding shows that the change of feed water pH throughout the filtration tests
254 was quite different at different initial feed water pH. When only PFHxA was added (initial pH: 3.3)
255 into the feed water, the pH of feed water kept decreasing throughout the filtration test due to the
256 concentration of PFHxA. However, when the initial pH of feed water was adjusted to pH 7.0, the pH
257 of feed water throughout the filtration was changed slightly. After adjusting the initial pH of feed
258 water to 10.0, the pH of feed water decreased significantly first and then kept between 7.0 and 8.5.
259 Such kind of change may be caused by two factors: co-ion competition effect and the dissociation of

260 PFHxA. When NaOH was added into the feed water, there are mainly three kinds of ions presented
261 in the feed water, including Na^+ , OH^- , $\text{CF}_3(\text{CF}_2)_4\text{COO}^-$. OH^- is smaller than $\text{CF}_3(\text{CF}_2)_4\text{COO}^-$ and
262 has higher mobility. Thus, it can penetrate through the membrane much more easily than
263 $\text{CF}_3(\text{CF}_2)_4\text{COO}^-$ and lead to a decrease of feed water pH. Additionally, the percentage of PFHxA
264 dissociated also may change at different concentrations. Therefore, the pH of feed water changed
265 significantly throughout the filtration.

266

267 3.2 Membrane flux of two NF membranes

268 The membrane flux of both NF 270 and NTR-7450 throughout the filtration test under different
269 filtration conditions were shown in **Fig.3**. It can be found that, under three kinds of testing
270 conditions, flux of NF 270 was more stable than that of NTR-7450. When the initial pH is 3.3, the
271 flux of NF 270 has a slightly decrease at the end of filtration, which might be caused by the
272 concentration polarization or membrane fouling. After adjusting the initial pH of feed water to 7.0
273 and 10.0, the flux did not change so much throughout the filtration. The membrane flux was even
274 increased after filtrating for some time when the initial pH of feed water was 10.0. However, for
275 NTR-7450, the membrane flux keeps decreasing throughout the filtration test when the initial pH of
276 feed water was 3.3. After increasing the initial pH of feed water to 7.0, the flux became stable
277 during the whole filtration. When the initial pH of feed water became 10.0, the flux even increased

along with the filtration. Based on above information, it can be concluded that increasing the pH to neutral or alkaline conditions can enhance the flux performances of membranes.

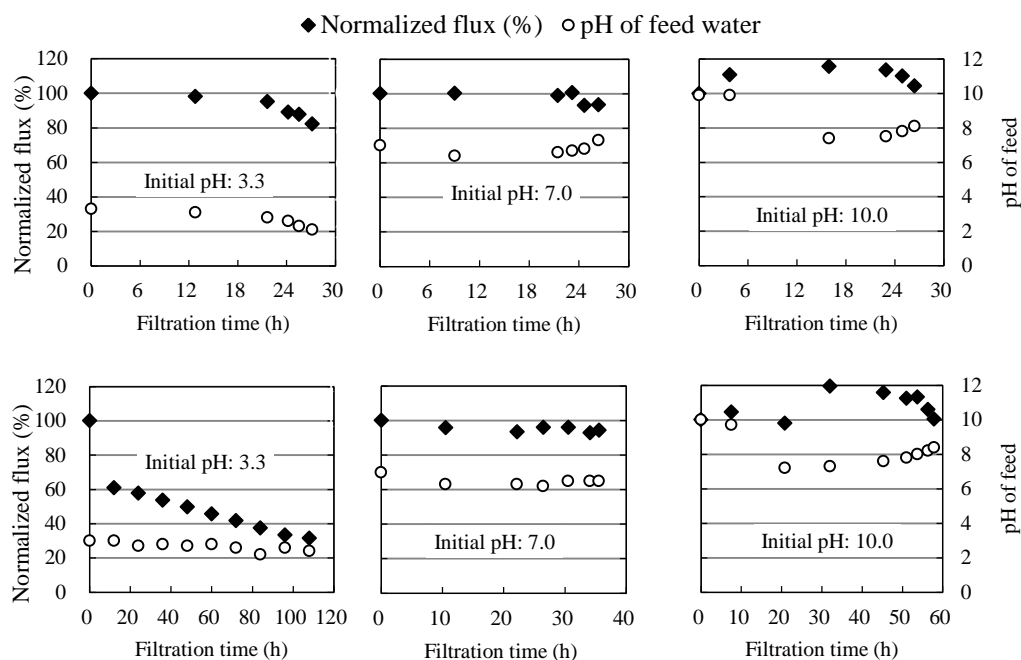


Fig. 3 Membrane flux of NF 270 and NTR-7450 throughout the filtration tests at different initial feed water pH conditions

As stated in introduction, a typical structure of NF membrane consists of three parts. Among these three parts, top selective layer has the most significant impact on membrane flux performance as it is the tightest layer of NF membrane. The top selective layer is a three dimensional network of polymer chains. Thus, NF membranes do not have real pores but just free volume inside the polymer chain network (Mänttari et al., 2006). As the polymer chains contain dissociable functional groups,

291 the conformation of polymer chains at different pH was quite different. Thus, membrane flux of NF
292 membrane at different pH was also quite different.

293

294 At all pH condition tested (Initial pH 3.3, 7.0 and 10.0), NF 270 was charged and the conformation
295 of polymer chains was expanded as a result of electrostatic repulsion between polymer chains. This
296 is the reason why the flux of NF 270 was not changed by the change of feed water initial pH.

297

298 However, for NTR-7450, its selective layer was made from sulfonated polyethersulfone, which
299 possesses dissociable sulfonate groups. According to the data reported by Mänttari et al., 2006, it
300 showed negative surface charge and seems did not have IEP. Increasing the pH of feed water might
301 promote the dissociation of sulfonate groups on membrane surface and the membrane “pores” can
302 be more open, leading to flux increase finally. In contrast, decreasing the pH of feed water may
303 depress the dissociation of sulfonate group and leading to the shrinkage of polymer chains, which
304 could lead to the flux decline finally. Additionally, Mänttari et al., 2006 also investigate the
305 hydrophilicity of NTR-7450 at different pH. They found that this membrane became very
306 hydrophobic at acidic conditions. Thus, the low membrane flux of NTR-7450 at initial pH 3.3 might
307 be caused by the shrinkage of membrane selective layer and the intrinsic hydrophobicity of
308 membrane surface. Once the initial pH of feed water was increased to 7.0 and 10.0, the sulfonate
309 groups became ionized and the membrane surface became more hydrophilic, which could reduce the

resistance for water to pass through the membrane. Thus, the membrane flux of NTR-7450 increased and kept constant throughout the filtration.

4. Conclusions

In conclusion, PFHxA in aqueous solution was concentrated successfully by two commercially available NF membranes. The impact of initial feed water pH on the rejection performances of NF membranes was investigated. The flux of polyamide NF membrane (NF 270) kept stable when changing the initial feed water pH. But its rejection rate to PFHxA was greatly enhanced once the initial feed water pH was increased from 3.3 to 7.0 or 10.0. However, opposite results were obtained with sulfonated polyethersulfone NF membrane (NTR-7450). It showed very high stability on rejection rate of PFHxA (>94.0%) while changing the initial feed water pH. But its membrane flux was sensitive to the change of initial feed water pH. When the initial feed water pH was increased from 3.3 to 7.0 and 10.0, the flux was increased significantly. The mechanism behind these phenomena was also discussed. The findings reported in this study could provide some useful guides for process design in treating industrial wastewater containing PFHxA.

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